(2)

REPORT DOCUMENTATION PAGE

AD-A205 241

1b RESTRICTIVE MARKINGS

3 DISTRIBUTION/AVAILABILITY OF REPORT
Approved for public release; distribution unlimited.

2b DECLASSIFICATION/DOWNGRADING SCHEDULE

4 PERFORMING ORGANIZATION REPORT NUMBER(S)

5 MONITORING ORGANIZATION REPORT NUMBER(S)
ARO 22394.5-CH

6a NAME OF PERFORMING ORGANIZATION
University of Minnesota
Department of Chemistry

6b OFFICE SYMBOL (If applicable)

7a NAME OF MONITORING ORGANIZATION
U. S. Army Research Office

6c ADDRESS (City, State, and ZIP Code)
207 Pleasant St. S.E.
Minneapolis, MN 55455

7b ADDRESS (City, State, and ZIP Code)
P. O. Box 12211
Research Triangle Park, NC 27709-2211

8a NAME OF FUNDING/SPONSORING ORGANIZATION
U. S. Army Research Office

8b OFFICE SYMBOL (If applicable)

9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
DAAG29-85-K-0074

8c ADDRESS (City, State, and ZIP Code)
P. O. Box 12211
Research Triangle Park, NC 27709-2211

10 SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO	PROJECT NO	TASK NO	WORK UNIT ACCESSION NO

11 TITLE (Include Security Classification)
Diffusion of Small Molecules in Bulk Polymers and Polymer Solutions Near the Glass Transition Temperature by Forced Rayleigh Scattering (unclassified)

12 PERSONAL AUTHOR(S) Lodge, Timothy Patrick

13a TYPE OF REPORT	13b TIME COVERED	14 DATE OF REPORT (Year, Month, Day)	15 PAGE COUNT
Final	FROM 3-15-85 TO 9-15-88	12-19-88	4

16 SUPPLEMENTARY NOTATION
The view, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

17 COSATI CODES		
FIELD	GROUP	SUB-GROUP

18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
Diffusion; glasses; polymer solutions; forced Rayleigh scattering

19 ABSTRACT (Continue on reverse if necessary and identify by block number)

The transient optical grating technique of forced Rayleigh scattering has been used to follow the diffusion of photochromic dye molecules in polymer solutions, both above and below the glass transition temperature. The results are largely in accord with free volume theories. However, the absolute magnitude of the diffusion coefficient at the glass transition temperature is a remarkably strong function of composition.

20 DISTRIBUTION/AVAILABILITY OF ABSTRACT
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS

21 ABSTRACT SECURITY CLASSIFICATION
Unclassified

22a NAME OF RESPONSIBLE INDIVIDUAL

22b TELEPHONE (Include Area Code) | 22c OFFICE SYMBOL

DD FORM 1473, 84 MAR 83 APR edition may be used until exhausted
All other editions are obsolete

SECURITY CLASSIFICATION OF THIS PAGE
UNCLASSIFIED

ARO 22394.5-CH

DIFFUSION OF SMALL MOLECULES IN BULK POLYMERS AND POLYMER SOLUTIONS NEAR THE GLASS TRANSITION TEMPERATURE BY FORCED RAYLEIGH SCATTERING

FINAL REPORT

PROFESSOR TIMOTHY P. LODGE

DECEMBER 13, 1988

U.S. ARMY RESEARCH OFFICE

GRANT NUMBER DAAG29-85-K-0074

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The technique of forced Rayleigh scattering (FRS) has been applied to the measurement of the diffusion of probe photochromic dyes in polymer solutions, particularly in the vicinity of the glass transition temperature, T_g. In addition to the information gained relative to mechanisms of diffusion in this regime, a great deal of progress has been made in the implementation of the experiment itself.

We have examined dye diffusion (various dyes) in polystyrene/toluene, polystyrene/ethyl benzene, poly(vinyl acetate)/toluene, polystyrene/tricresyl phosphate, polystyrene/-Aroclor 1248, and polymethyl methacylate/methyl methacrylate solutions, as well as bulk poly(vinyl acetate), poly(vinyl butyral), and poly(ethylene glycol). Our primary interest has been the composition and temperature dependence of diffusion, especially near T_g. We have compared data obtained in poly(vinyl acetate)/toluene over the entire composition range with theory, and in particular found that the Vrentas-Duda free volume model can describe the data extremely well without the use of arbitrary adjustable parameters.

We have reported the first measurements of diffusion as a function of temperature through the glass transition in solution, and find the results to be in qualitative accordance with free volume models. Furthermore, a most interesting result has emerged, namely, that the value of the diffusion coefficient at T_g is an extremely strong function of composition. Thus, the mobility of a penetrant molecule may increase by five orders of magnitude as a diluent is added, even while the temperature is reduced to keep the solution as a macroscopic glass. Then, upon the addition of still further diluent, the mobility begins to drop, until in pure glassy diluent the mobility is less than in pure glassy polymer. This observation will form the basis of the next phase of our research.

Under the course of the grant we have developed a second FRS apparatus to improve the net rate of data acquisition. Furthermore, an extensive computer-controlled optical shutter system has been implemented to permit reliable extraction of diffusion coefficients down to 10^{-16} cm^2/s. A new interferometer geometry has been designed, which reduces the diffusion distance to one-half micron.

In many solutions, an unusual signal decay form is routinely observed. This has been unambiguously assigned to the mutual interference between diffracted waves from gratings due to each photoisomer. Detailed analysis of these decays allows simultaneous extraction of the two photoisomer diffusion coefficients, with the correct assignment of which isomer is the more mobile. (There is some degree of misconception about this in the literature, and other workers have routinely mis-interpreted their data).

The key to successful FRS measurements lies in the choice of photochromic probes with suitable properties. We have devoted a great deal of effort to this problem, and have pioneered the use of Aberchrome 540 as a new FRS probe with almost ideal characteristics. We have also demonstrated how probes like methyl red, which are used frequently in the field, can interact with hydrogen-bond accepting sites on polymer chains to give misleading results.

We have utilized pulsed-field gradient NMR measurements of diffusion in support of some of our FRS work, particularly to confirm our assignment of which dye isomer is the more mobile, and in unravelling the hydrogen-bond interactions in the methyl red/poly(vinyl acetate) system.

Our current and future work, in addition to the study of diffusion at T_g over the complete composition range, will focus on two new problems. One is the measurement of diffusion in a reactive system, for which our model will be the free radical polymerization of methyl methacrylate. The other is the potentially anisotropic diffusion in microstructured polymer environments, such as microphase-separated block copolymer melts, and liquid crystalline polymer systems.

12-11-88